Hydrogen from electrochemical reforming of ethanol assisted by sulfuric acid addition

Ana B. Calcerrada, Ana R. de la Osa, Javier Llanos, Fernando Dorado,
Antonio de Lucas-Consuegra*

Departamento de Ingeniería Química, Facultad de Ciencias y Tecnologías Químicas, Universidad de Castilla-La Mancha, Avenida Camilo José Cela 12, 13071 Ciudad Real, Spain

ABSTRACT

The addition of H_2SO_4 to the anolyte feeding solution for the electrochemical reforming of ethanol has been studied in terms of activity and stability for hydrogen production in a PEM electrolysis cell. Five equivalent MEAs based on commercial Pt-Sn/C and Pt/C as anode and cathode materials, respectively, and a Nafion membrane, have been prepared and tested to optimize the addition of the H_2SO_4. Results demonstrated that the addition of an optimal H_2SO_4 concentration (ethanol $4\,mol\,L^{-1}$ and $0.01\,mol\,L^{-1}$ H_2SO_4) enhances the electrocatalytic activity and stability of the MEA by decreasing the energy requirements for hydrogen production. According to impedance spectroscopy experiments, this improvement is caused by a decrease in the anodic charge transfer resistance, probably due to an increase in the number of contact triple points (electrolyte/catalyst particles/electronic support). However, the addition of a higher H_2SO_4 concentration ($0.05\,mol\,L^{-1}$) induced the dissolution of the Pt-Sn/C anodic catalyst causing a severe degradation of the MEA. Therefore, the optimal addition of H_2SO_4, which is not consumed during the electrochemical reforming experiments, may be of great practical importance for using this technology for the renewable hydrogen production from real bioethanol streams.

1. Introduction

In the last years, hydrogen production has emerged as a promising alternative to replace fossil fuels as energy resource, due its cleaning and sustainable energy system [1,2]. Hydrogen production is mainly based on catalytic steam reforming (SR), Water Gas Shift (WGS) or partial oxidation (PO) processes, which result in a mixture of H_2/CO gas diluted with CO_2, steam and N_2. Among the different carbon energy sources including biomass, alcohols or Natural Gas (NG), this latter is usually selected as the reference fuel for hydrogen production in industrialized countries, owing to its low cost and widespread infrastructure. All this kind of processes and molecules requires from separation and purification stages upstream the reactors to obtain pure hydrogen.

In response, water electrolysis is known to face some of these challenging aspects since it can generate clean and friendly hydrogen in a single reaction/separation step [3,4]. However, water electrolysis technology suffers from high energetic requirements e.g. $50–60\,kWh\,kg_{H2}^{-1}$ and hence, novel alternatives should be found.

A variation of the conventional water electrolysis method is the electrochemical reforming (or electrolysis) of organic solutions. This technique allows to produce pure hydrogen from different kind of aqueous solutions of biomass-derived molecules such as: alcohols, aldehydes or organic acids [5]. In the electrochemical reforming process, a typical PEM reactor configuration is used. It is based on a membrane electrode assembly (MEA), which is formed by an anode/polymeric electrolyte/cathode, analogous to that in low temperature PEM fuel cells. However, in the electrochemical reforming, the electrical power supplied by an external source is used to split the organic molecules. The electro-oxidation of the organic molecule occurs at the anodic catalyst leading to the production of intermediate oxidation products, electrons and protons (H^+). These protons are transported to the cathodic side through the polymeric electrolyte membrane and then, protons and electrons (the latter driven through the external circuit) recombine for the production of hydrogen gas [6]. Previous works were found to study the electrochemical reforming of a wide variety of water-alcohol mixtures, i.e. methanol [4,6–9], glycerol [10–12], ethanol [1,6,13–17], second generation industrial bio-ethanol [18], ethylene glycol [2] and iso-propanol [6] at temperatures typically below 90 °C. Among then, ethanol aqueous solutions are the most

M E A	EtOH	H$_2$SO$_4$	pH
	mol·L^{-1}		
1	4	0	4.00
2	4	0.005	2.30
3	4	0.01	2.25
4	4	0.005	2.20
5	4	0-0.05	-

Linear Voltammetry T = 50 ºC → Chronopotentiometry experiments at different currents, T = 50 ºC, for 36 h → Linear Voltammetry T = 50 ºC → Anode characterization after electrochemical reforming tests (XRD, TGA, AA)

Comparison of the polarization curves

→ Electrochemical Impendance spectrosopy measurements at each anolyte feeding stream composition, T = 50 ºC
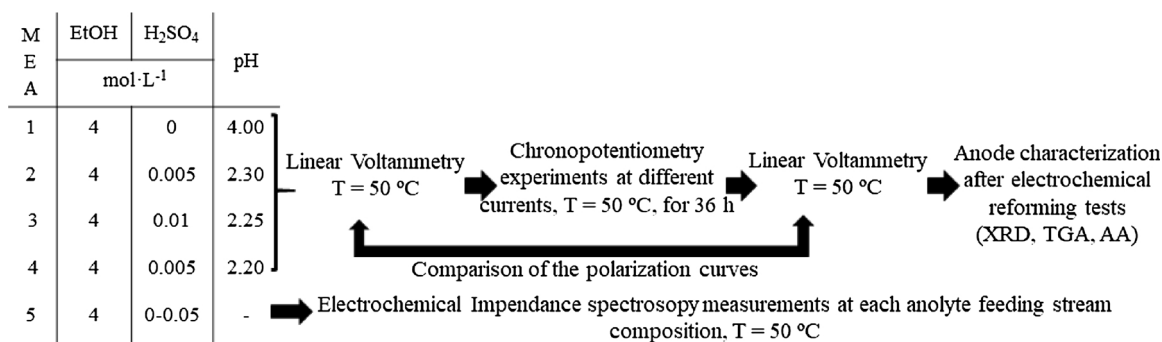
Fig. 1. Scheme of the overall experimental procedure performed with the different MEAs.

interesting ones, due to their easy storage, safety conditions and almost direct production from biomass [18,19]. Concerning the different screened electrodes, Pt anodic catalysts are the most stable and active ones for the organic molecule electro-oxidation reaction in acid media. In this sense, the addition of a second metal (Ru, Sn) promotes the reaction, decreases the surface poisoning effect and in some cases, reduces the cost of the anodic catalyst [20–22]. As a general conclusion, Electrochemical Reforming is a very interesting technique for direct hydrogen production, which requires a much lower energy demand than that of water electrolysis and catalytic reforming processes, as analyzed in a previous work [23]. Furthermore, the electrochemical reforming of ethanol could be used for portable hydrogen production applications or as a complement to renewable energies, such as wind or solar power [24,25]. However, a common limitation of all these previous works is the low current density values obtained, which led to very high electrode area requirements, thus limiting the practical application. Hence, further research is clearly needed to improve the obtained current density values.

In the present work, a systematic and deep study has been performed on the addition of H$_2$SO$_4$ to the anolyte feeding solution for the electrochemical reforming of ethanol, in order to improve the activity and stability of the membrane electrode assembly (MEA). To that purpose, five equivalent MEAs based on commercial Pt-Sn/C and Pt/C as anode and cathode materials, respectively ensambled on a Nafion membrane, have been prepared and tested under different electrochemical reforming conditions in order to optimize the anolyte composition. Each MEA has been tested following the same experimental protocol, which included linear voltammetry and chronopotentiometry measurements. In addition, in-situ (impedance spectroscopy) and ex-situ (X-ray diffraction, thermogravimetric analysis) characterization techniques have been performed to support the obtained electrocatalytic results.

2. Experimental

2.1. Membrane electrode assembly (MEA) preparation

Electrochemical reforming tests were carried out in a PEM electrolysis cell unit described in detail elsewhere [18]. Commercial Pt-Sn supported on carbon vulcan XC-72 (20% Pt-Sn/C, 3:1 Pt:Sn atomic ratio, Premetek Co.) and Pt supported on carbon black (20% Pt/C – Alfa Aesar) were used as the anodic and cathodic catalysts, respectively. Both catalysts were coated on Carbon Paper Substrates (Fuel Cell Earth), used as gas diffusion layers, by depositing the corresponding catalyst inks, composed by a mixture of the catalyst powder with a Nafion solution (5 wt.% Sigma Aldrich) and isopropanol (99.9% for HPLC, Sigma Aldrich) as solvent. The metal loading was 1.5 mg cm^{-2} for the anode and 0.5 mg cm^{-2} for the cathode, being the geometric surface area of both electrodes 6.25 cm^2. A proton exchange Nafion membrane (Hidrógena Desarrollos Energéticos) of 185 μm thickness was used as the solid electrolyte. The membrane electrode assembly

(MEA) was then prepared by pressing together all these elements applying a load of 1 ton at 120 ºC for 3 min. A total of five equivalent MEAs have been prepared for this study in order to perform the different electrocatalytic and characterization tests as will be explained below.

2.2. Electrocatalytic experiments

Electrochemical measurements were carried out using a Vertex 5A.DC potentiostat-galvanostat (Ivium Technologies). An ethanol solution of 4 mol L^{-1}, acidified with sulfuric acid at 4 different concentrations (0, 0.005, 0.01, 0.05 mol L^{-1}), was supplied to the anodic chamber of the cell, at a constant flow rate of 8 mL min^{-1}, using a peristaltic pump (Pumpdrive 5001, Heidolph). Water was fed to the cathodic chamber at a constant flow rate of 3 ml min^{-1} using the same multichannel peristaltic pump. The operation mode was discontinuous, i.e., recirculating both streams to the feed reservoirs, whose volumes were 1 and 0.5 L for the anode and cathode chambers, respectively. Electrolysis experiments were performed at a fixed temperature of 50 ºC. Hydrogen production rates were quantified by means of electrical current measures and verified by a gas volumetric flowmeter. The purity of the obtained hydrogen was confirmed offline using a gas chromatograph (Bruker 450 GC). As mentioned above, a series of four MEAs was used to study the influence of the acidification of the anolyte. To that purpose, each MEA was tested according to the following protocol of experiments (schematized on Fig. 1) under a different feed composition:

1. Linear voltammetry experiments at 50 ºC and 5 mV s^{-1} scan rate up to a maximum applied potential of 1.4 V.
2. Chronopotentiometry experiments at 50 ºC, extended for 36 h, to study the stability and possible degradation of the system. Each experiment consists of six different cycles of 6 h developed at different applied currents (varying from 0.1 A–0.35 A) with an open circuit potential step (of 5 min of duration) between each cycle.
3. Repetition of the linear voltammetry test in order to compare polarization curves obtained before and after the mild term chronopotentiometry tests.
4. The used MEA was removed from the electrochemical reactor unit and then the anode was transferred to be checked by the postmortem characterization techniques described in the next section.

Additionally, a fifth fresh MEA was prepared to carry out Electrochemical Impedance Spectroscopy (EIS) measurements under the different explored anolyte feeding conditions. EIS was performed using the impedance module of the Ivium potentiostat/galvanostat described above at a potential of 0.5 V. The cell impedance spectra was recorded using a frequency range from 10 kHz to 10 mHz with a potential amplitude of 10 mV at 50 ºC.

*2.3. Physicochemical characterization of the anode after the electrocatalytic tests*

X-ray diffraction analysis (XRD) corresponding to the anode of each tested MEA were performed by a Philips model X'Pert MPD with Co-filtered Cu Kα radiation (λ = 1.54056 Å) (Philips, Eindhoven, The Netherlands). XRD diffractograms, which were compared to that related to fresh anode, were recorded over a 2θ range from 15° to 80° at scan rate of 5 °C min^{-1}. In addition, the anode was characterized by Thermogravimetric analysis (TGA) in a TGA apparatus (TGA-DSC1, METTLER). The sample was heated under air atmosphere (100 mL min^{-1} flow rate) from room temperature to 800 °C (5 °C min^{-1} heating rate) and then it was kept at the latter temperature for 4 h in order to completely removed the carbon.

3. Results and discussion

3.1. Influence of the addition of H$_2$SO$_4$ on the electrochemical reforming of ethanol

Firstly, in order to study the effect of the addition of an acid electrolyte (H$_2$SO$_4$) on the electrocatalytic activity of the system, a preliminary set of linear voltammetry experiments was conducted at a constant temperature of 50 °C and a scan rate of 5 mV s^{-1}, using different anolyte feeding solutions. Fig. 2a) shows the variation of the current density with the applied potential (0–1.4 V range) under four different anolyte streams: i) water, ii) 0.01 mol L^{-1} H$_2$SO$_4$ aqueous solution, iii) 4 mol L^{-1} ethanol aqueous solution and, iv) 4 mol L^{-1} ethanol acidified with 0.01 mol L^{-1} H$_2$SO$_4$ aqueous solution. Fig. 2b) depicts hydrogen production rate theoretically calculated via Faraday's law and experimentally measured vs. the applied potential obtained for ethanol (4 mol L^{-1}) and ethanol (4 mol L^{-1}) + H$_2$SO$_4$ (0.01 mol L^{-1}) anodic solution experiments.

From Fig. 2a) a negligible electrocatalytic activity can be observed for the experiments performed in absence of ethanol, i.e., exclusively feeding water or 0.01 mol L^{-1} H$_2$SO$_4$ solution to the anode. However, the system showed a certain electrocatalytic activity under the presence of ethanol both as a 4 mol L^{-1} ethanol solution or acidified by H$_2$SO$_4$ (4 mol L^{-1} ethanol + 0.01 mol L^{-1} H$_2$SO$_4$ anolyte feeding solution). These results confirmed that neither water nor H$_2$SO$_4$ solution were electrolyzed at the explored electrical potential range, being only the electrochemical oxidation of ethanol molecules, which occurred at the explored conditions. Hence, in good agreement with previous studies [1,18], ethanol electro-oxidation starts at electrical potentials close to 0.6 V. This value is much lower than the electrical potential typically required for PEM water electrolyzers (around 1.5 V), where hydrogen production in the cathode behaves as a dynamic hydrogen electrode (DHE) [9]. Therefore, it is clear that under the studied conditions, ethanol is the unique source for H$_2$ production, being the electro-oxidation of the organic molecule the principal process occurring at the anode. Previous works have already shown that acetaldehyde and acetic acid are the main obtained electro-oxidation products due to the difficulty for breaking the C−C bond under the explored conditions [14–26]. Therefore, the incomplete electrochemical oxidation path is also the most likely one, even under presence of H$_2$SO$_4$ in the anodic feed, via reactions (1 and 2):

$$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2\,e^- \tag{1}$$

$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + 4\,e^- \tag{2}$$
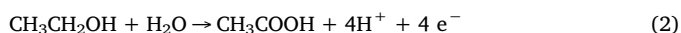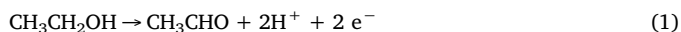
On the other hand, it can be observed that electrocatalytic activity of the system was improved by the addition of 0.01 mol L^{-1} of H$_2$SO$_4$ to the parent ethanol anolyte solution, achieving current density values up to 100 mA cm^{-2} at a cell potential of 1.4 V. This effect, which will be investigated in detail below, is in good agreement with a previous work of Sapountzi et al. [6], who already demonstrated a positive effect of
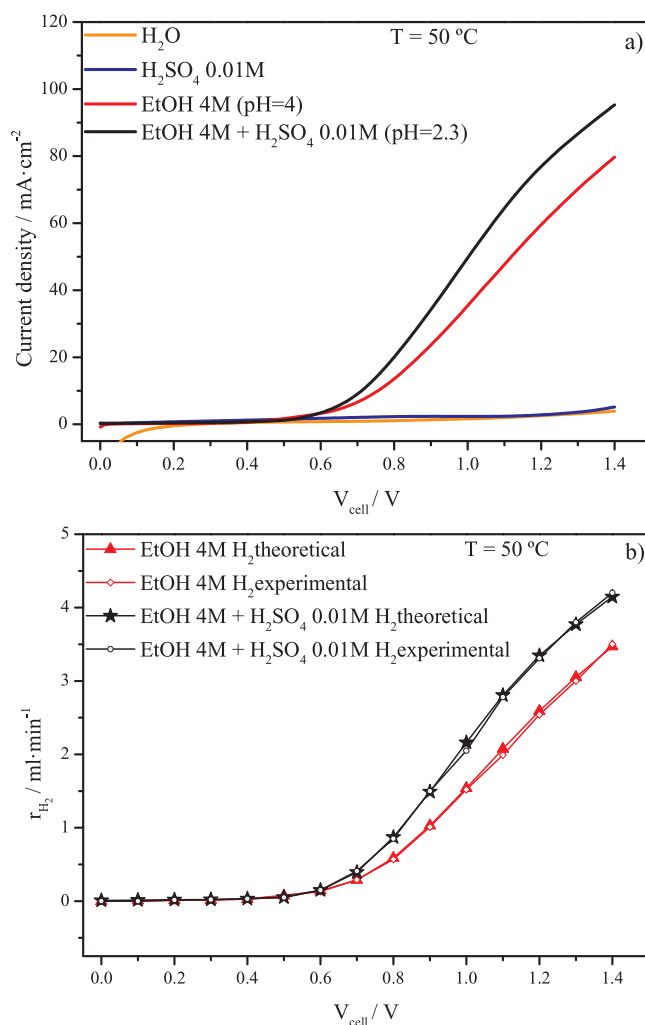

Fig. 2. Linear voltammetry at 50 °C and 5 mV s^{-1} under different anolyte feeding solutions: a) water, H$_2$SO$_4$ 0.01 mol L^{-1}, Ethanol 4 mol L^{-1} and Ethanol 4 mol L^{-1} + H$_2$SO$_4$ 0.01 mol L^{-1} and b) theoretical and experimental hydrogen production rates for Ethanol electrolysis under: 4 mol L^{-1} and Ethanol 4 mol L^{-1} + H$_2$SO$_4$ 0.01 mol L^{-1}.

the ethanol electro-oxidation reaction when changing the anolyte pH from 7 to 0.4 by the addition of H$_2$SO$_4$.

It is also interesting to note that obtained current density values could be directly related to the hydrogen production rates collected in the cathode of the PEM cell [1]. Hence, it can be observed from Fig. 2b) that theoretical hydrogen production rates, calculated via Faraday's law, were experimentally confirmed by separate gas-volumetric measurements of hydrogen flows at each applied potential for the experiments performed under presence of ethanol on the anolyte feeding solution. It demonstrated that practically 100% of the applied electrical energy was used for hydrogen production. In addition, a hydrogen purity of 99.999% was verified by offline gas-chromatography analysis, demonstrating the feasibility of using the electrochemical reforming for the production of a pure hydrogen stream in a single reaction and separation step [16]. Finally, it is also clear that an increase in the applied potential leads to higher current densities values in all cases, which implies higher hydrogen production rates [1,13,18].

3.2. Comprehensive study of electrocatalytic performance and degradation behavior

In order to investigate the stability and possible degradation of the system, a mild-term chronopotentiometry experiment was carried out at 50 °C to each prepared MEA. The test consists of 6 cycles of 6 h each,
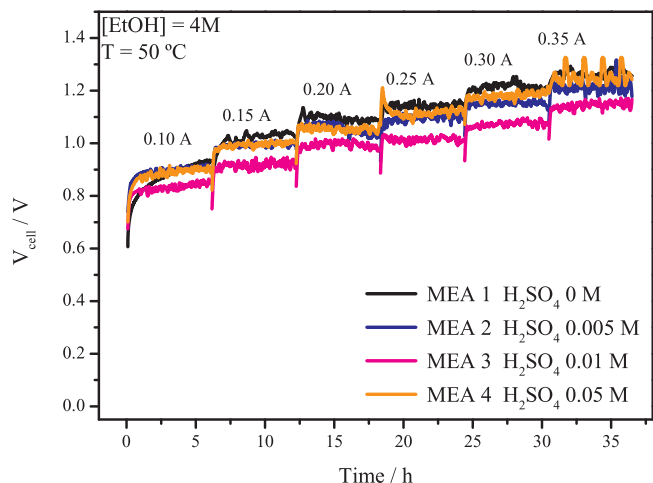
Fig. 3. Chronopotentiometry experiments at different currents for the different MEAs.

Fig. 4. Nyquist plots obtained from the impedance spectra under different feeding anolyte solutions: using Ethanol $4 \, mol \, L^{-1}$ and different H_2SO_4 concentration from 0 to $0.05 \, mol \, L^{-1}$ at 50 °C at constant 0.5 V potential and under the application of frequencies from 10 kHz to 10 mHz with a potential amplitude of 10 mV.

Table 1
Ohmic resistance and combined mass and charge transfer resistance calculated from the Nyquist plot of the impedance spectra.

[EtOH] = $4 \, mol \, L^{-1}$		Ohmic R_S/Ohm	$R_{CT} + R_{MT}$/Ohm
[H_2SO_4]	$0 \, mol \, L^{-1}$	0.231	6.32
	$0.005 \, mol \, L^{-1}$	0.236	5.75
	$0.01 \, mol \, L^{-1}$	0.228	4.62
	$0.05 \, mol \, L^{-1}$	0.232	5.27

developed at a constant current, which is varied from 0.1 to 0.35 A along cycles, with an open circuit step of 5 min between them.

Fig. 3 shows the cell voltage variation vs. time for four equivalent MEAs, each one explored under a different feeding solution composition, as described on the experimental section. A similar trend of the potential vs. time curve was observed on each galvanostatic step. An important initial increase of the potential occurred during the first 1–2 h of operation at each applied current. In agreement with other studies, it could be attributed to the adsorption of the C_2s hydrocarbons reaction products of ethanol electro-oxidation, such acetaldehyde or acetic acid, which may decrease the number of Pt-Sn active sites for the main electrochemical reaction [13,26]. From this point on the system seemed to attain an almost steady-state voltage value that led to a stable operation of the cell. By comparison of results obtained by using the MEA under the four different scenarios, it can be observed that the addition of H_2SO_4 enhanced the electrocatalytic activity of the system up to an optimal concentration of $0.01 \, mol \, L^{-1}$. However, further addition of H_2SO_4 ($0.05 \, mol \, L^{-1}$) led to an increase of the cell potential at fixed current, showing a decrease in the electrochemical reforming activity. Therefore, there is a clear optimal value of pH (around 2.25), which enhances the electrocatalytic activity of the system. Prior to explain in detail the origin of this optimal composition, it should be mentioned that there was not an important variation of the following solution parameters measured on the anolyte reservoir along the 36 h of the experiment (see figures of the Supporting Information): pH (Fig. S1), conductivity (Fig. S2) and sulfates ions concentration (Fig. S3). It suggested that H_2SO_4 was not consumed during the electrolysis experiments promoting the ethanol electro-oxidation reaction on the anode of the cell.

Fig. 4 shows the results of the impedance spectra recorded at 50 °C to a new freshly prepared MEA (MEA 5) at each of the following previous anolyte solution compositions: Ethanol $4 \, mol \, L^{-1}$ + H_2SO_4 (0–$0.05 \, mol \, L^{-1}$) and presented in form of the Nyquist plot. As already reported in previous studies [6,26], two semicircles were observed in the Nyquist plots of the EIS, which can be related to the cathodic (first semicircle at higher frequencies) and anodic reactions (second semicircle at lower frequencies). It can be observed that the cathodic charge transfer resistance (determined by the difference between the high and low frequency intercepts of the first semicircle with the x-axis on the Nyquist plots) is almost negligible vs. the second semicircle, indicating that hydrogen evolution is a facile reaction in contrast with the anodic one. This is also in very good agreement with a previous work [6] where the authors have identified a negligible cathodic overpotential contribution on a similar configuration for ethanol electro-reforming by using a AgCl reference electrode. Table 1 shows ohmic resistance values calculated from the high frequency region and the combined mass and
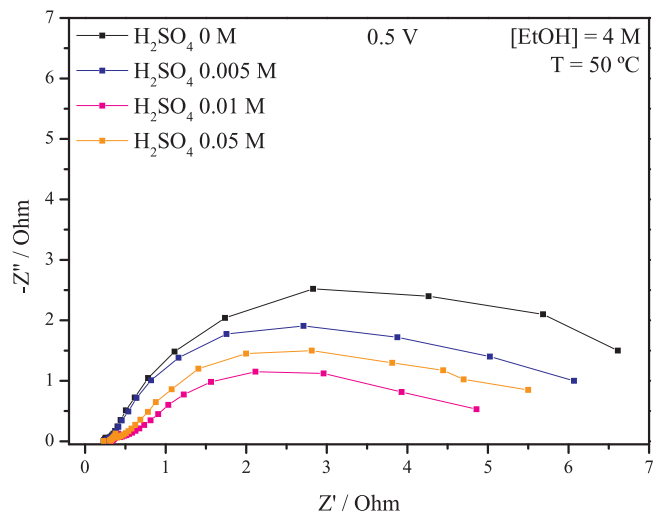
charge transfer resistance calculated from the low frequency region. According to previous studies, the ohmic resistance has been mainly attributed to the resistance of the membrane. On the other hand, the combined mass and charge transfer resistance has been mainly attributed to the anodic charge transfer resistance [26–28], considering the absence of mass transfer limitations (as can be observed from the polarization curves) and the much lower cathodic overpotentials values vs. the anodic ones of the explored system [6].

Firstly, it can be observed that acidification by H_2SO_4 does not change the membrane resistance and therefore, ionic conductivity of the membrane is not modified by the addition of the acid anolyte. However, the addition of H_2SO_4 up to a concentration of $0.01 \, mol \, L^{-1}$ was found to decrease the anodic charge transfer resistance. Therefore, it is clear that the observed improvement on the electrochemical reforming activity by the addition of H_2SO_4 (as shown on Fig. 4) can be exclusively attributed to an enhancement of the anodic charge transfer reaction kinetics. According to these results, the existence of an optimal pH value could be explained in terms of two countervailing effects. Previous studies have shown that the electro-oxidation rate of alcohols is favored by increasing the pH [29–31]. However, Sapountzi et al. [6] pointed out that an increase in the ionic conductivity of the anolyte solution by decreasing the pH may lead to an extended reaction anodic zone. It may lead to an extra pathway for protons to move increasing the number of contact triple points (electrolyte/catalyst particles/electronic support), which enhances the anodic electro-oxidation reaction. Both opposite effects may explain the existence of an optimal pH value (2.25), which lead to the lowest anodic charge transfer resistance and the highest ethanol electro-reforming activity as shown on the experiments collected in Fig. 3.

Continuing with the experimental protocol explained on the experimental section, in order to study the stability and degradation of the MEA due the presence of different H_2SO_4-ethanol solutions, linear
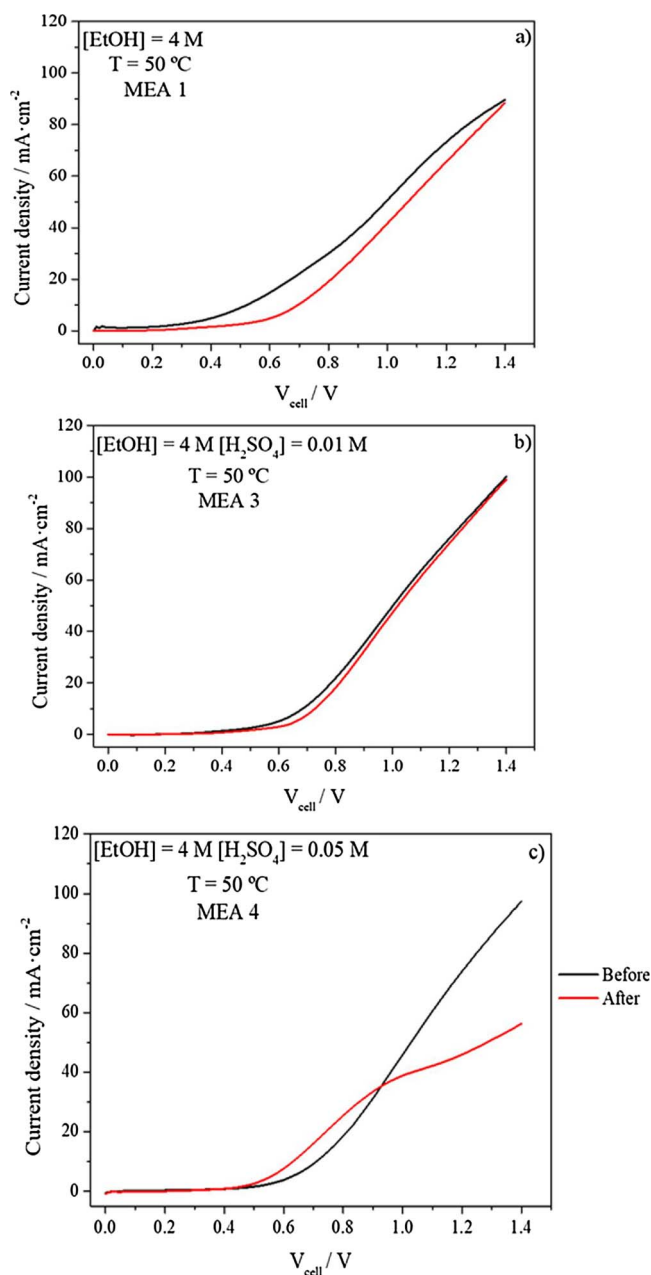
Fig. 5. Linear voltammetry tests before and after the chronopotentiometry experiments for MEA 1, MEA 3 and MEA 4.

voltammetry tests were also performed after the mild-term durability tests (for comparison purposes with the fresh MEA). Fig. 5 shows the comparison of the polarization curves before and after the chronopotentiometry experiments for the representative MEAs (MEA 1, MEA 3 and MEA 4). A slight degradation of the MEA can be observed in the experiment run in absence of H_2SO_4 (MEA 1), while this degradation becomes much more important under presence of H_2SO_4 0.05 mol L^{-1} (MEA 4). However, MEA degradation was almost negligible in case of MEA 3, working under presence of H_2SO_4 0.01 mol L^{-1} (the current-potential curves were almost the same before and after the chronopotentiometry experiments for 36 h). It has been shown that osmosis is the most important driving force for the membrane swelling process, being the swelling of the Nafion membrane lower under presence of H_2SO_4 in comparison with the presence of H_2O [32]. Therefore, the addition of H_2SO_4 on the experiments with MEA 3 may decrease the swelling degree of the membrane improving its stability along the mild term experiment of Fig. 4. However, it can be observed that the

addition of a higher concentration of H_2SO_4 led to an important difference on the linear voltammetry curves shown on Fig. 5c) (MEA 4). Hence, a strong degradation of the MEA is clearly observed, which could be related to the oscillatory behaviour of this MEA on the last cycle of the chronoamperometry (Fig. 3) under the constant current application of 0.35 A. It is also interesting to note the positive effect of the optimal H_2SO_4 addition to the anolyte feed stream on the MEA 3. In this case, by comparison of linear voltammetry curves at 80 mA cm^{-2} obtained after the chronoamperometry (for MEA1 and MEA3), an important decrease of the energy requirements for hydrogen production (Fig. S4) can be calculated from 37.52 kW h kg$_{H2}$$^{-1}$ to 29.75 kW h kg$_{H2}$$^{-1}$. This improvement effect of 21% on the energy requirement, caused by addition of an optimal amount of H_2SO_4, may be of great practical importance when using this technology especially with real bio-ethanol streams, typically characterized by pH values below 4.

3.3. Anode characterization after electrochemical reforming experiments

Pt-Sn/C anodic catalysts were characterized after chronopotentiometry experiments and then compared to the fresh sample, which was equivalently prepared only for characterization purposes, by different characterization techniques.

Fig. 6 depicts XRD analysis of both fresh and used Pt-Sn anodic electrode from MEAs 1, 3 and 4. Typical diffraction peaks of Pt and C were clearly observed. In good agreement with previous studies [13], no peaks corresponding to Sn were observed due its poor crystallinity. However, a decrease of the intensity of the diffraction peaks can be observed in case of MEA 4, which was tested with the highest H_2SO_4 concentration (0.05 mol L^{-1}). It seems to indicate that, on this latter case, the presence of a high concentration of sulfuric acid may lead to a considerable dissolution of the metal loading deposited on the carbon paper, then removing part of the active phase for the ethanol electro-oxidation reaction, which may explain the strong degradation observed in Fig. 5.

On the other hand, Fig. 7 shows the thermogravimetric analysis developed under air atmosphere for the same anodic catalysts. It can be observed that the fresh anode and those used in MEAs 1 and 3 show a weight loss of around 92%. This weight loss corresponds to the removal of carbon coming from both the catalyst support and the gas diffusion layer and NAFION indicating that, in these three cases, a final value of around 8% of metal (Pt-Sn) loading was kept on the sample. However, thermogravimetric characterisation of the anode on MEA 4, tested under the highest H_2SO_4 concentration, revealed that only around 1.5% metal remained on the catalyst after the electrocatalytic tests.
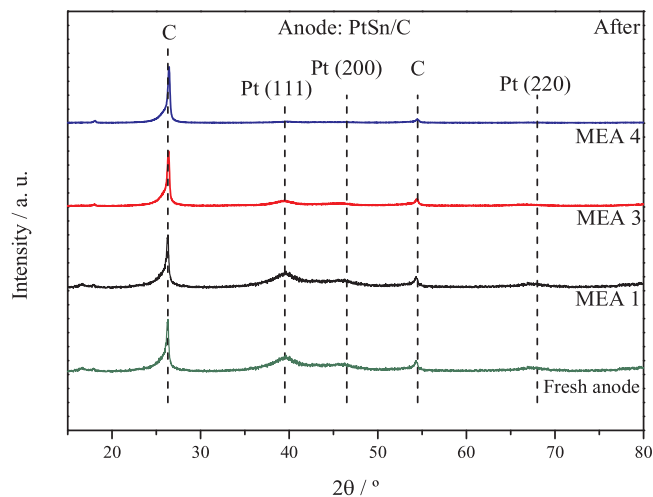

Fig. 6. XRD patterns of the Pt-Sn/C anodes before (fresh) and after the electrocatalytic experiments of the different MEAs.
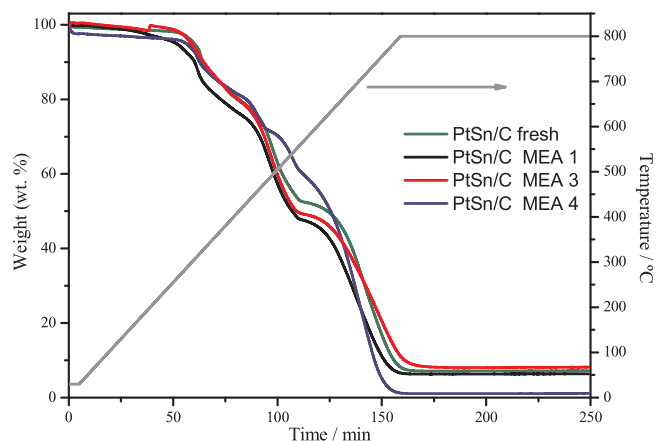
Fig. 7. TGA experiments of the Pt-Sn/C anodes before (fresh) and after the electrocatalytic experiments. Conditions: air atmosphere (flow rate $= 100 \, \text{mL min}^{-1}$), from room temperature to 800 °C (5 °C min^{-1}) keeping at 800 °C during 4 h.

Considering the same initial content of Pt, Sn, Carbon and NAFION on the four electrodes and the similar TGA results on the electrodes coming from MEA 1 and 3 with a completely fresh electrode, the differences in the electrode coming from MEA 4 could be ascribed to an initial lower metal content. It corresponds to a partial loss of the nominal loading by prior dissolution in the over-acidified anolyte. Therefore, in good agreement with XRD results, TGA analysis confirmed a strong dissolution of the Pt-Sn/C anodic catalyst in MEA 4, treated under H$_2$SO$_4$ 0.05 mol L^{-1}, which would explain the degradation behaviour shown on Fig. 5.

4. Conclusions

The following conclusions could be drawn from this study:

- The addition of an optimal concentration of an acid electrolyte such as H$_2$SO$_4$ enhances the activity and stability of a Pt-Sn/C-Nafion-Pt/ C (anode-solid electrolyte-cathode) membrane electrode assembly used for the renewable hydrogen production from electrochemical reforming of ethanol.
- H$_2$SO$_4$ added to the anolyte solution is not consumed neither electrolyzed at the explored conditions, being ethanol the unique source for hydrogen production via ethanol electro-oxidation.
- The addition of H$_2$SO$_4$ does not improve the ionic conductivity of the electrolyte but decreases the anodic charge transfer resistance up to an optimal value. It can be attributed to two countervailing effects: the increased kinetics of ethanol electrooxidation at higher pH values and an extended reaction anodic zone induced by the H$^+$ on the solution at lower pH values.
- The addition of H$_2$SO$_4$ enhances the stability of the MEA up to an optimal concentration of 0.01 mol L^{-1}. A higher concentration of H$_2$SO$_4$ close to 0.05 mol L^{-1} results in the dissolution of the active phase of the anodic catalyst.
- The addition of an optimal H$_2$SO$_4$ concentration allows the operation for mild working times by decreasing the energy requirement for ethanol electrolysis in more than 20% at high current density values ($\sim 100 \, \text{mA cm}^{-2}$).

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi: https://doi.org/10.1016/j.apcatb.2018.03.028.

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